

AS ORIGINALLY FILED**5 Polymers and plastics with long-lasting odor and the use thereof**

The invention relates to a process for preparing odorant polymers and plastics, to the odorant polymer or the odorant plastic itself, and also to a molding composition 10 and an article which comprise the odorant polymer or the odorant plastic.

For some time the prior art has included efforts to prepare odorant plastics. Considerable practical problems arise here. If the intended plastic is mixed with the required amount of a desired odorant, such as a perfume, and the mixture is then 15 processed to give moldings, most of the odorant evaporates or is thermally degraded. In relation to the proportion of the odorant which actually remains within the plastic, there is also the risk that the odorant will separate out from the plastic once the latter has cooled and solidified. This results in migration of the odorant to the surface of the solidified plastic, giving the surface a "greasy", 20 unsightly and disfigured appearance. This process also inevitably results in high losses of the expensive odorant.

In order to eliminate these disadvantages, it is known in the prior art, via DE-A-16 94 055, that a silicon dioxide powder as carrier material can be mixed 25 with a liquid odorant until the resultant mixture forms small clumps. Further silicon dioxide powder with a lower apparent density than the silicon dioxide initially used is added to these clumps, giving small clumps of dimensions not greater than 0.05 mm. These are then mixed with the plastic.

30 A disadvantage of this process is that the plastic processed in this way comprises an inorganic solid which can adversely affect the physical properties of the plastic, for example impact strength and transparency.

DE-A-37 21 916 begins with pulverulent porous carrier materials whose origin 35 may be either inorganic or organic, in the form of plastics or of plastics mixtures.

The desired odorant is adsorbed onto the porous carrier material and mixed with a plastic for further processing by, for example, extrusion.

- During the processing of the plastics the odorant diffuses into the polymer matrix.
- 5 A disadvantage here is that this diffusion of the odorant into the polymer matrix during processing can also lead to loss of the odorant, since the porosity of the particular carrier material means that the odorant is adsorbed in the pores of the carrier, rather than absorbed.
- 10 It is an object of the present invention, taking this prior art as a starting point, to provide a process which allows cost-effective preparation of odorant polymers, in particular of odorant plastics with long lasting odor, and to provide these odorant polymers and this odorant plastic.
- 15 We have found that this object is achieved by means of a process in which a comminuted or fine-particle first polymer material, in particular a plastic, is mixed with a desired odorant, allowed to swell for a predetermined period, and then further processed under a predetermined pressure and at a predetermined temperature. Since the comminuted or fine-particle first polymer material is mixed
- 20 and allowed to swell with the desired odorant for a predetermined period, the odorant can enter into every one of the particles of the first polymer material. The polymer particles are genuinely loaded with the odorant. Correspondingly, for the purposes of the present invention swelling is the absorption of the odorant into the polymer matrix or, respectively, the polymer network of the first polymer, which is used as a carrier. A precondition for this is that the distribution of the odorant in the first polymer material is uniform. In the case of macroporous materials - as in the prior art - what is obtained is merely pores charged with odorant, without any loading of the polymer skeleton. If the odorant has sufficient thermal stability, the resultant odorant polymer or plastic can be further processed in a usual manner by
- 25 melting followed by homogenization. Particular further processing methods for odorants of relatively low thermal stability are given at a later stage in this text.
- 30

- In one preferred embodiment of the process of the invention, after the first polymer material has been allowed to swell with the odorant it may be mixed with a second plastic and then melted and then homogenized. This gives a compact material which comprises the odorant polymer material together with the second plastic, the

macroscopic distribution being approximately uniform. For the purposes of the present invention, the first and second material are differentiated by referring to the first as the polymer material, the carrier material, and the second as the plastic, the objective here being to make it clear that the first polymer material may be, but 5 does not have to be, a thermoplastic.

The second plastic may likewise have been comminuted, but this is not an essential requirement.

- 10 The first polymer material and the second plastic may be identical or differ from one another. If the first polymer material is identical with the second plastic, then for the purposes of the present invention the second plastic may also be a polymer material which is not a plastic. This method gives an odorant polymer. If the first polymer material, which serves as actual carrier material for the odorant, differs 15 from the second plastic, the first polymer material in particular comprises a plastic in the form of a particulate, crosslinked plastic or of an elastomer, which may also have rubbery properties, with a glass transition temperature T_g below the glass transition temperature T_g of the second plastic, preferably 0°C or below, particularly preferably below -10°C .
- 20 The way in which first polymer materials of this type can be saturated with the particular odorants used is that they form a microscopically small network which absorbs the odorants, whereupon the odorants swell the network. The odorant used may be an odorant oil. A particular use of the polymers or plastics prepared by the 25 process of the invention becomes possible if the odorants used comprise pheromones and/or ecomones. Plaques coated or saturated with pheromones have hitherto been used with promising results for controlling insects. Since pheromone traps of this type are mostly employed in the open, these products are exposed to weathering and therefore have to be frequently replaced since the active ingredient 30 is leached out. By employing the process of the invention it is possible to incorporate these odorants into the particular plastic provided so that the odorants are protected from the effects of weathering and can be used in the form of boards, plaques, or other moldings with a lasting odor. The process of the invention for preparing odorant polymers or plastics is therefore not restricted to those polymers 35 or plastics providing an odor detectable by the human smell, but also encompasses

odorant polymer or plastics whose odor can be detected only by the sensitive olfactory systems of animals, in particular of insects.

- The mixing of the first polymer material with this odorant or odorant oil may be
5 carried out in a closed container. This ensures that all of the odorant oil is available
for the loading of the first polymer material, rather than being dissipated into the
environment. Examples of materials suitable for preparing the powder of the first
polymer material are spray-dried dispersions of polymer or of plastic.
- 10 Depending on the nature of the odorant used, in particular on its thermal stability,
the first operation consisting of mixing the first polymer material in powder form
with the odorant and allowing it to swell may be followed, in the further operation
to form the odorant polymer or plastic, by process modifications individually
matched to the odorant. The second plastic here may be used in ground, powder, or
15 pellet form.

In the case of odorants with very low thermal stability, the method of further
processing may be that once the first polymer material has been allowed to swell it
is mixed with the second plastic at high pressure at about room temperature or by
20 way of slight heating to below the glass transition temperature T_g of the second
plastic, preferably to just below T_g . The second plastic material used is then
preferably one which melts at a low temperature, the phenomenon of cold flow
being utilized. The second plastic may be the same as the first polymer material but
may also differ therefrom. A procedure such as that described is particularly
25 suitable for pheromones or ecomones in general.

In the case of odorants which have little or no sensitivity to high temperatures,
once the first polymer material has been allowed to swell it may be mixed with the
second plastic again at high pressure and with heating to a temperature which is
30 above the glass transition temperature T_g either of the first polymer material or of
the second plastic, preferably just above T_g in each case.

However, in the case of odorants which have no particular sensitivity to high
temperatures it is quite possible to provide conventional pressure conditions and
35 temperature conditions during processing, e.g. by extrusion. The mixture of the
odorant-loaded first polymer powder and the second plastic, e.g. in the form of

pellets, may then be melted and homogenized in a mixing assembly at atmospheric pressure and at an elevated temperature. The melting in the mixing assembly may, for example, be carried out in an extruder or kneader. After homogenization, the resultant melt may be pelletized and further processed by the usual methods of processing for thermoplastic molding compositions.

- Materials preferably used as first polymer material are thermoplastics, thermoplastic elastomers, graft rubber, polymers based on renewable raw materials, or polymers or polymer mixtures based on starch. It is particularly preferable for the first polymer material to be selected from polylactic acid, as an example of a polymer based on renewable raw materials, polyurethanes, polyamides, polyesters, or polybutylene terephthalates, or polymers, copolymers, block polymers, triblock copolymers, or graft copolymers of styrene, butadiene, acrylonitrile, (meth)acrylate, or acrylic esters. The abovementioned materials are also suitable for use as second plastic, and in that case it is also possible to use mixtures of these with polycarbonates. Examples of the abovementioned polymers, copolymers or triblock copolymers are polystyrene (PS), in particular here impact-modified polystyrene, polybutadiene, polyacrylates, polymethyl methacrylates (PMMA), acrylonitrile-butadiene-styrene copolymers (ABS), acrylonitrile-styrene-acrylate copolymers (ASA), styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers (SBR), acrylonitrile-butadiene copolymers (NBR), and styrene-butadiene-styrene triblock copolymers (SBS). Good results are also achieved using ground superabsorber material.
- The first polymer material may be in the form of a dewatered emulsion polymer, for example, obtained either by spray drying or by coagulation and drying. Fine-particle polymer powders obtained by precipitation from solutions are also highly suitable as first polymer material.
- The invention also provides the odorant polymer or the odorant plastic itself, obtained by the process of the invention. For simplicity, the text below refers to odorant plastics, and this is intended to include the possibility that the materials used produce an odorant polymer which is not a plastic. The odorant plastic may be in pellet form and an example of its use is in defense against animals. For the purposes of the present invention, animals may be pests, in particular including insects. However, defense against animals includes the repelling of domestic

animals, such as dogs, cats and other small animals from places which they would like to foul but where this fouling is undesirable. Pellets made from the odorant plastic may preferably be used here, and particularly preferably pellets made from biodegradable plastics and loaded with the appropriate odorants which are known per se and repel the animals. Examples of these biodegradable plastics are polymers based on renewable raw materials, for example polylactic acid, and polymers and polymer mixtures based on starch or based on synthetic materials, for example based on polyesteramides or on branched polyesters. The advantage of using the odorant plastic of the invention is that the active ingredient is dissipated over a long period and cannot be removed from the plastic even by rain.

The invention further relates to a molding composition which comprises an odorant polymer of this type or an odorant plastic of this type. Depending on the proportion of odorant in the finished plastic, which may be in the form of pellets, for example, this may also be used as a masterbatch. The relatively high proportion of odorant may be achieved, for example, by altering the mixing ratio of first polymer material and second plastic.

The invention also relates to the use of the molding composition which comprises an odorant polymer or an odorant plastic, or the use of the odorant polymer or plastic itself for altering and/or improving the odor properties of articles. There is a wide variety of applications available here, and particular advantage is given by those which conceal the unavoidable unpleasant intrinsic odors of plastics in a wide variety of applications. An example which may be mentioned here is the interior of motor vehicles in which components produced from plastic, for example dashboard supports, center consoles, trim films, etc. can have a strong odor of the plastic when they are new. Using the odorant plastics or the molding compositions prepared therefrom, this unpleasant odor can be concealed. Since the skilled worker is aware of a very broad range of very varied odorants, all of which can be incorporated into the plastic by the process of the invention, a varied range of possibilities is available to automobile manufacturers. Examples which may be mentioned here are plastics with the odor of leather, fresh air, flowers, forest or perfume.

Another possible application consists in concealing unpleasant intrinsic odors of construction materials, for example in the window frame sector or the baseboard

sector. Here, too, in the first weeks after completion the intrinsic odors occurring are regarded as unpleasant and may be concealed, for example using a citrus odor.

- Other articles manufactured from plastic, such as vacuum cleaner housings or
- 5 plastic parts in refrigerators, may have an unpleasant odor of the plastic from which they have been produced, such as an ABS plastic or an impact-modified polystyrene. These odors, too, may be concealed by a wide variety of desired types of odor, using odorant plastics.
- 10 The invention also provides an article which comprises the odorant polymer or the odorant plastic and/or comprises the molding composition in which the odorant polymer or the odorant plastic is present. This article may be a plastic part or a semifinished product, for example an injection molded article, or a film, sheet, pipe, or profile. There are many uses for the article, which has at least some inbuilt
- 15 odor due to the odorant polymer or plastic present therein. Firstly, it may be used for the uses described above for the odorant polymer or the odorant plastic and for the molding composition which comprises the odorant polymer or odorant plastic. Secondly, however, it may be used for improving room air quality. It then acts as an odor dispenser, and it is advisable here to avoid any excessive proportion of the
- 20 odorant present in the plastic, so that the article generates an odor which is discrete and only just detectable when in use in office areas or other living areas. However, a higher proportion of the odorant may be indicated if the article used as odor dispenser is employed in the sanitary sector. If the article has been produced by injection molding, it may advantageously be given any desired shape. For example,
- 25 it is possible to produce lemons with the odor of lemons or coniferous trees which give out an odor of spruce needles, or any desired other article with its associated odor characteristics. These odorant articles are therefore also suitable as decorative articles.
- 30 Another possibility is to incorporate the odorant plastic into articles in daily use, such as household articles, telephones, computer casings, etc. The corresponding odorants may be selected so as to provide a motivation to purchase, or to generate a general feeling of wellbeing, or else even to increase the ability to concentrate. It is also possible for promotional items, such as ballpoint pens or other small
- 35 products, to be provided with a customer-specific odor, these articles comprising the odorant plastic or the molding composition which comprises the odorant

plastic. In addition, it is possible to produce odorant greeting cards, CD packaging, cassette packaging, telephone cards, or chip cards.

- If the articles are produced in the form of sheeting, they may be used as packaging
- 5 films, as self-adhesive odorant labels for refrigerators, for example to eliminate fishy odors, or for wardrobes or other storage boxes. It should be emphasized that the selection of the appropriate odorant also allows long lasting defense against pests. For the purposes of the present invention, the term pest has a wide meaning, including insects and also small animals, such as mice, rats, martens, etc. Use of
- 10 the appropriate odorants permits appropriate repellent cable-insulation materials to be used in electrical engineering. It is not just cable-insulating material which may be brought into consideration here, but any construction material liable to attack by small animals. In relation to the defense required against insect pests, mosquitoes and ants are worthy of consideration, as are various moth species.
- 15 Examples of the uses mentioned for the odorant plastic, or the molding composition or article comprising the odorant plastic are so varied that they can only be illustrated here by way of example. The use can also be extended to any desired other sectors of daily life. For example, selection of a suitable odorant
- 20 plastic also permits the production of toys with a variety of aromas.

The invention will be described in more detail below by way of examples.

- Example 1:
- 25 The first polymer material is composed of a spray-dried polybutadiene and polyacrylate rubber. 200 g of this dried rubber was placed in a 1 000 ml screw-top glass container and mixed with 10 or 20% of the odorant citral or citronellol. The glass containers were then rolled on a roller bed for 48 h. This mixed the odorant
- 30 uniformly into the rubber.

- The rubber treated in this way was blended firstly with a styrene-acrylonitrile polymer with a melt index MVI (220°/10 kg) of 62 g/10 min, at a concentration of 10 or 20%, and secondly with nylon-6 with a melt index MVI (275°/5 kg) of
- 35 120 g/10 min, in the same mixing ratio. Then each rubber-pellets mixture was

compounded in an extruder with contrarotating screws. The machine parameters here were set as follows:

Screw rotation rate: 200 rpm
Temperatures: Feed: 30°C,
5 Processing unit: 220°C
Throughput: 1.5 kg/h

The experiments carried out under Example 1 are shown in Table 1.

10 Example 2:

In this example the first polymer material is composed of a graft rubber dried in a fluidized-bed dryer and prepared as described in DE-B-24 27 960. MgSO₄ was used for precipitation, followed by preliminary dewatering to a water content of about 28% by centrifuging. 100 parts of this graft rubber were treated with 25 parts 15 of citronellol and mixed as described in Example 1.

40 parts of the graft rubber pretreated in this way were intimately mixed with 60 parts of a styrene-acrylonitrile copolymer melt (SAN) at 230°C in an extruder 20 with corotating screws. The acrylonitrile content in the SAN melt was 35%. This gave a melt with a strong lemon odor, and the melt was used to produce moldings, such as plaques and bars, which continued to have a strong lemon odor. Films were also produced.

25 The resultant moldings were subjected to an odor test at intervals of a number of months. Even after a storage time of 10 months here, it was still possible to detect a pronounced lemon odor.

Example 2a:

30 The mixture of Example 2 made from the graft rubber and the citronellol was mixed with SAN in such a way that only about 30% of the odorant-saturated graft rubber was present in the finished mixture. This mixture, too, had a strong lemon odor.

35

The odor test was again undertaken over a period of a number of months. After 10 months here there was still a discrete, pleasant fruity odor.

Examples 2-1 to 2-7:

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Odorant plastics of the invention were prepared as described in Example 2 from other polymer materials and plastics given in Table 2, using the odorants also given in that table.

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Table 1:

Experiment	1st Polymer material	Odorant	Amount %	2nd Plastic material	Con-stituent amount %*	Color
1	Polybutadiene	Citral	10	Styrene-acrylonitrile polymer	10	Slightly yellowish
2	Polybutadiene	Citral	10	Styrene-acrylonitrile polymer	20	Slightly yellowish
3	Polybutadiene	Citral	20	Nylon-6	10	Brownish yellow
4	Polybutadiene	Citral	20	Nylon-6	20	Brownish yellow
5	Polybutadiene	Citronellol	10	Styrene-acrylonitrile polymer	10	Very slightly yellowish
6	Polybutadiene	Citronellol	10	Styrene-acrylonitrile polymer	20	Very slightly yellowish
7	Polybutadiene	Citronellol	20	Nylon-6	20	Very slightly yellowish
8	Polybutadiene	Citronellol	20	Styrene-acrylonitrile polymer	10	Very slightly yellowish
9	Polyacrylate	Citral	10	Styrene-acrylonitrile polymer	20	Very slightly yellowish
10	Polyacrylate	Citral	10	Nylon-6	10	Slightly yellowish
11	Polyacrylate	Citral	20	Nylon-6	20	Yellowish
12	Polyacrylate	Citral	20	Nylon-6	20	Yellow-orange
13	Polyacrylate	Citronellol	10	Styrene-acrylonitrile polymer	10	Yellow-orange
14	Polyacrylate	Citronellol	10	Styrene-acrylonitrile polymer	20	Slightly yellowish
15	Polyacrylate	Citronellol	20	Nylon-6	10	Slightly yellowish
16	Polyacrylate	Citronellol	20	Nylon-6	20	Slightly yellowish

*) Relates to the proportion of the first loaded polymer material in the mixture with the second plastic

Table 2:

No.	1st Polymer material	Odor	Amount introduced % by weight	2nd Plastic	Mixing ratio polymer: plastic	Remarks
2-1	Polybutadiene-g-SAN	Nerolidol*	10	SAN	30:70	Floral odor, reminiscent of green timber
2-2	Polybutadiene-g-SAN	Phytol*	15	SAN	30:70	Sweet floral odor
2-3	Polybutadiene-g-SAN	Hydroxyciol*	20	ABS	20:80	Floral; powdery
2-4	Polybutadiene-g-SAN	Geranyl acetate*	15	ABS	25:75	Fresh rose odor
		70-30				
2-5	Polybutadiene-g-SAN	Alfa-Ionon-100*	10	ABS	30:70	Floral/woody
2-6	Polybutadiene-g-SAN	2-Phenylethanol	15	PMMA	40:60	Transparent, floral odor, rose
2-7	Polybutadiene-g-SAN	N,N-Diethyl-m-toluamide	15	SAN	30:70	Repels mosquitoes

*) Chemical name in Table 2a

Table 2a:

Odorant BASF trade name	Chemical name
Nerolidol	3,7,11-Trimethyldodecatrien-3-ol
Phytol	3,7,11,15-Tetramethylhexadec-2-en-1-ol
Hydroxyciol	3,7-Dimethyloctane-1,7-diol
Geranyl acetate	Mixture of 70% geranyl acetate and 30% neryl acetate
Alfa-Ionon 100	4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-buten-2-one

Example 3

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The materials and odorants given in Table 3 were used to repeat the preparation of the mixture of Example 1 from the graft rubber and the odorant oil. The materials mentioned under 3-11 to 3-14 are fully biodegradable polymers. The odorants used are sensitive to high temperatures.

10

Once each odorant had been mixed into the first polymer material, this material was mixed with each of the pulverulent or pelletized plastic given and compressed into a mold under mild conditions, with heating to just above the glass transition temperature T_g of the thermoplastic used.

15

As an alternative to this, the mixtures resulting from the first polymer material and the second plastic were processed between heated rolls to give films.

20

In these versions of the process the processing temperatures selected were below the usual temperatures for extrusion, the extent about 50 to 150°C.

Table 3:

No.	1st Polymer material	Odorant	% by weight	2nd Plastic	Mixing ratio polymer: plastic	Remarks
3-1	Polybutadiene-g-SAN	Citronellol	20	SAN	10:90	Fruity odor, lemon aroma
3-2	Polybutadiene-g-SAN	Linalyl acetate*	10	ABS	25:75	Fruity, bergamot
3-3	Polybutadiene-g-SAN	Ethyl isovalerate	15	ABS	20:80	Fruity, grape, apple
3-4	Polybutadiene-g-SAN	Isoamyl acetate*	20	ABS	15:85	Fruity, peach, banana
3-5	Polybutyl acrylate-g-SAN	Acetoin*	15	ASA	10:90	Odor of butter, cream
3-6	Polybutyl acrylate-g-SAN	Cyclohexyl[ethyl] acetate	15	SAN	25:75	Fresh floral, raspberry
3-7	Polybutadiene-g-MMA	Tetrahydrolinalool*	10	SAN/PMMa	30:35:35	Translucent, floral, slightly woody
3-8	Polybutyl acrylate-g-SAN	2,6-Dimethyl-2-heptanol N,N-Diethyl-m-toluamide Piperonyl butoxide	10	ASA	20:80	Fruit odor, repels small animals, dogs, cats
3-9	Polybutadiene-g-SAN	Citronellol	15	ABS	30:70	Repels mosquitoes and dogs
3-10	Polybutadiene-g-SAN	Citronellol	20	ABS	20:80	
3-11	Polybutadiene-g-SAN	Citronellol + clove powder 1:1	20	Polylactic acid	10:90	
3-12	Denatured starch	Citronellol + clove powder 1:1	10	Polylactic acid	25:75	
3-13	Denatured starch		15	Polylactic acid	20:80	
3-14	Polylactic acid powder		10	Polyhydroxybutyrate-valerate copolymer	15:85	

* Chemical name in Table 3a

Table 3a:

Odorant BASF trade name	Chemical name
Linalyl acetate	3,7-Dimethyl-1,6-octadien-3-yl acetate
Isoamyl acetate	3-Methylbutyl acetate
Acetoin	3-Hydroxy-2-butanone
Tetrahydrolinalool	3,7-Dimethyloctan-3-ol

Example 4:

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The version of the process described in this example, cold pressing, can be used for odorant oils which are particularly sensitive to high temperatures. The effect utilized here is that many plastics begin to flow under high pressure even below their melting point.

- For this version of the process, the first polymer materials given in Table 4 were mixed with the odorant oils also given in Table 4 and allowed to swell until each odorant had become completely mixed into the first polymer material.

The second plastic used was the plastics given in Table 4, in the form of powder or fine regrind. Moldings were then pressed from this pulverulent mixture from 50 to 70°C under a pressure of 200 bar.

- 10 This process is particularly suitable for low-boiling pharmaceutically active substances, in particular naturally occurring substances. This version of the process is also highly suitable for the biodegradable polymers given in Examples 3-11 to 3-14 in Table 3, using the odorant oils which are also given in the table and are sensitive to high temperatures.

Table 4

No.	1st Polymer material	Odorant	% by weight	2nd Plastic	Mixing ratio polymer: plastic	Remarks
4-1	Polybutadiene-g-SAN	N,N-Diethyl-m-toluamide Pheromone	12	SAN powder	40:60	Repels mosquitoes
4-2	Polybutadiene-g-SAN	Repellents	2	ABS	20:80	Moth traps, attracts spe... moths
4-3	Polybutadiene-g-SAN	Pyrethrum extract + piperonyl butoxide	10	ABS	30:70	Repels dogs, cats
4-4	Polybutadiene-g-SAN	Chlorpyriphos	10	ABS	10:90	Insect poison
4-5	Polybutadiene-g-SAN	Azamethiphos	10	ABS	15:85	Moth agent
4-6	Polybutadiene-g-SAN	Lavender oil	10	ABS	20:80	Attracts flies
4-7	Polybutadiene-g-SAN	Spruce needle oil	15	ABS	20:80	Lavender oil odor
4-8	Polybutadiene-g-SAN		15	ABS	25:75	Spruce needle odor (odor dispenser)